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DETERMINATION OF VOLATILE THINNER IN OIL VARNISH

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I. INTRODUCTION

Almost all oil varnishes¹ contain, as thinner, gum spirits of turpentine, "mineral spirits,"² or a mixture of the two. Most of the turpentine substitutes prepared for use in paint and varnish are made from mineral oil. Benzene (C_6H_6) carbon disulphide, alcohol, and wood turpentine are very rarely used for oil varnish, though wood turpentine is frequently used in the manufacture of driers.

The definition for "volatile thinner," proposed by committee D-1 of the American Society for Testing Materials, is as follows: "All that liquid portion of a paint, water excepted, which is volatile in a current of steam at atmospheric pressure."³

¹ In this paper the term "oil varnish" means varnish containing fixed oil and resin.

² The term "mineral sprits" is being generally accepted for the petroleum distillates that are used as substitutes for turpentine.

³ Proc. Amer. Soc. for Testing Materials, 14, I, p. 225; 1914.

II. PURPOSE OF INVESTIGATION

Since there has appeared no published work in which different methods for the determination of volatile thinner have been compared by the analysis of samples containing turpentine and of samples containing mineral spirits, this investigation was undertaken in order to ascertain the accuracy and convenience of the different methods.

III. REVIEW OF THE LITERATURE

Mills⁴ stated that the volatile portion of a varnish can be determined by "simple evaporation with water." McIlheney⁵ was the first to investigate the subject systematically, but all the samples that he analyzed contained, as thinner, only turpentine. By direct distillation under reduced pressure he obtained results that were too low. By heating films of varnish at 100° C for three-quarters to one hour he obtained results for percentages of volatile thinner which, with two samples, were very close to the amounts actually present, and with a third sample were too low. By distilling off the turpentine from a 25 g. sample of varnish with a current of steam, separating the water in the distillate from the turpentine, and weighing the latter, he obtained satisfactory results. To correct his figures for the solubility of turpentine in water he added 0.3 g. to the weight of the former. Approximately 100 cc of water were condensed. He proposed this method for general use, stating that, besides being accurate, it has the advantage of leaving the nonvolatile portion in a condition that is suitable for further examination. Livache and McIntosh⁶ quoted McIlheney and recommended his method. Walker⁷ modified McIlheney's method by heating the still containing 100 g. of the varnish at 130° C, adding to the weight of the volatile thinner 0.3 g. for each 100 cc of condensed water. Sabin⁸ and Holley⁹ recommended the latter method. Wolff¹⁰ stated that in the steam distillation, heating the still containing the varnish at 110–115° C is necessary for complete distillation of the thinner. Brown¹¹ proposed a method for the determination of volatile thinner in insulating varnish, according to which 3 to 4 g. of the sample are

⁴ J. Soc. Chem. Ind., 5, p. 222; 1886.

⁵ J. Amer. Chem. Soc., 16, p. 344; 1894.

⁶ Livache and McIntosh, *Manufacture of Varnishes*, 3, p. 184; 1911.

⁷ Bull. 109, revised, Bur. of Chem., Dept. of Agriculture; 1910.

⁸ Bottler and Sabin, *German and American Varnish Making*, p. 250; 1912.

⁹ Holley, *Analysis of Paint and Varnish Products*, p. 23; 1912.

¹⁰ *Farben-Ztg.*, 17, p. 849, 1912.

¹¹ *Proc. Amer. Soc. for Testing Materials*, 14, p. 467; 1914.

dissolved in ether (or some other readily volatile solvent), the solution diluted to 50 cc in a graduated flask, and 10 cc of the solution are flowed from a pipette upon a weighed glass plate with a ground surface. The plate is kept at room temperature and weighed at intervals until no further loss occurs. If the varnish contains a "very active drier," the plate is kept in a current of illuminating gas. Brown also determines the specific gravity of the varnish and of the thinner, as obtained by distillation, and calculates the percentage by volume of thinner and "body" (nonvolatile portion). He claims for his method the advantage that by continuing to weigh the plate at intervals, one can determine the rate of oxidation of the film.

IV. EXPERIMENTAL

1. COLLECTION AND PREPARATION OF SAMPLES

Two samples of varnish were obtained from a reliable manufacturer, one being made from rosin, linseed oil, Chinese wood oil, driers, and "mineral spirits," and the other from a hard gum, hardened rosin, linseed oil, Chinese wood oil, driers, and turpentine. These samples are subsequently designated as *A* and *B*, respectively. An examination of the distillate obtained from *B* showed that it contained a very small amount (about 2 per cent) of "mineral spirits." Two samples of varnish were prepared in the laboratory, the nonvolatile portion of both consisting of approximately equal parts by weight of calcium resinate (prepared by heating rosin with 5 per cent of its weight of slaked lime) and boiled linseed oil (containing lead and manganese). In one case the thinner used was turpentine, and in the other light mineral oil. These samples are designated as *C* and *D*, respectively. Examination of the distillates obtained from *A* and *B* and of the thinners used to prepare *C* and *D* gave the results shown in Table I. The distillation was made with an Engler apparatus.¹² The light mineral oil that was present in *A* and *D* is fairly representative of mineral-oil varnish thinners.

¹² T. B. Stillman, *Engineering Chemistry*; 1897.

TABLE 1
Results of Examination of Thinners

Material	Specific gravity at 15.6 15.6° C	Refractive index at 20° C	Unpolymerized residue	Refractive index of unpolymerized at 20° C	Initial boiling point	90 per cent distilled at—	95 per cent distilled at—
			Per cent		°C	°C	°C
Distillate from A.....	0.763	1.423			119	175	187
Distillate from B.....	.864	1.470	2.5	1.473			
Thinner used for C.....	.869	1.471	1.2	1.513			
Thinner used for D.....	.761	1.425			118	178	190

2. DETERMINATION OF VOLATILE THINNER BY DIFFERENT METHODS

Four methods were used for the determination of the amounts of volatile thinner in *A*, *B*, *C*, and *D*.

Method 1.—A steam distillation was made, using 100 g of varnish, the still containing the varnish being heated to 115–120° C in an air bath. The distillation required from one and one-fourth to one and one-half hours and the volume of water condensed varied from 550 to 700 cc. The distillate from the varnish was separated from the water and weighed. The “corrected” results (see Table 2) were obtained by adding to the weight of the volatile thinner 0.3 g for each 100 cc of water condensed.

Method 2.—Approximately 1.5 g of varnish were placed in a stoppered glass vial and the vial and contents weighed. The varnish was poured into a weighed metal dish, having a circular flat bottom 8 cm in diameter, the stopper was replaced, and the vial and stopper weighed. The dish was heated in an air bath at 110–115° C until no further loss in weight occurred. The maximum time required was three hours. The loss was assumed to be volatile thinner.

Method 3.—Brown’s method. (See p. 2.) With *A* and *B* a mixture of ether and chloroform was used, but *C* and *D* dissolved readily in ether. The films obtained were very uneven, being thickest at the edges of the plates. The plates were placed in a dust-free glass-walled cabinet with free access of air. The plates were weighed at intervals until no further loss occurred. The maximum time required was three hours. The loss was assumed to be volatile thinner.

Method 3a.—This was the same as Method 3, except that the plates were kept in a current of illuminating gas. The maximum time required was three hours.

Method 4.—A small stoppered vial containing about 1 g of varnish and a small camel's-hair brush were weighed together. The contents of the vial were poured upon a weighed glass plate, 10 by 15 cm, and brushed out to a thin film. The stoppered vial and brush were then weighed. The films of varnish weighed 0.6 to 0.9 g. The plates were allowed to stand in the cabinet used for Method 3 and were weighed at intervals until no further loss occurred. The first weighing was made at the end of two hours and subsequent weighings showed that no further loss occurred in any case. The loss was assumed to be volatile thinner.

The temperature of the room during the determinations by Methods 3, 3a, and 4 varied from 30–35° C.

The results obtained by all methods are shown in Table 2.

TABLE 2

Results of Determination of Volatile Thinner by Different Methods

Method	Sample A, mineral spirits		Sample B, turpentine		Sample C, 50.1 per cent turpentine present		Sample D, 53.9 per cent mineral spirits present	
	Found	Mean	Found	Mean	Found	Mean	Found	Mean
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
No. 1.....	50.0		52.5		48.9		52.7	
	49.2	49.6	53.5	53.0	49.5	49.2	53.0	52.9
	51.7		54.4		51.0		54.7	
No. 1 (corrected).....	51.3	51.5	55.4	54.9	50.2	50.6	54.9	54.8
	49.1		52.9		50.0		53.3	
No. 2.....	49.6	49.4	52.7	52.8	49.2	49.6	52.3	52.8
	48.7		51.8		49.3		53.4	
No. 3.....	48.7	48.7	51.0	51.4	49.0	49.2	52.8	53.1
	48.6		52.6		49.2		53.0	
No. 3a.....	49.3	49.0	52.2	52.4	50.0	49.6	52.9	53.0
	49.1		52.8		49.5		53.3	
No. 4.....	49.1	49.1	52.6	52.7	49.6	49.6	53.4	53.4
Mean.....		49.5		52.9		49.6		53.3
Maximum deviation from mean.....	+2.2	+2.0	+2.5	+2.0	+1.4	+1.0	+1.6	+1.5
Maximum deviation from known.....					-1.1	-0.9	-1.6	-1.1

V. DISCUSSION OF RESULTS AND METHODS

The uncorrected results obtained by method 1 and those obtained by methods 3, 3a, and 4 are all as concordant as can be expected. It was also to be expected that slightly higher figures would be obtained by method 3a than with method 3. The percentages of volatile thinner in C and D obtained by method 1

(uncorrected) and by methods 2, 3, 3a, and 4 are but slightly less than the amounts actually present and the corrected results by method 1 are but slightly greater. It appears, therefore, that for such varnishes the most convenient method may be selected for routine use. During the application of varnish the thinner is rapidly evaporating, so that for practical purposes an error of 1 per cent in the determination is of no significance. In this laboratory method 2 is used, the result being reported as the whole percentage next above the figure obtained. Should the steam distillation method be used, with subsequent correction of results, the percentage of volatile thinner should be reported as the whole percentage next below the figure obtained. In the examination of samples of interior, floor, coach, and spar varnishes panel tests and drying tests on glass are made separately instead of in connection with the determination of volatile thinner as is suggested by Brown. The distillate obtained by steam distillation of an unweighed portion of the varnish is used for the determination of the nature of the thinner.

The practically complete volatilization of the thinner in a short time, as obtained in the determinations by method 4, indicates that with such samples it is highly improbable that the nature of the dried film, or the rate of drying, is influenced by the nature of the thinner. These samples, however, were analyzed shortly after preparation, while some varnishes of high quality are aged, sometimes for years, before being marketed. In aged varnishes it is probable that turpentine changes so as to yield nonvolatile material, which remains in the varnish coat, when the film dries. The changes in the volatile thinner contents of varnishes on aging is under investigation in this laboratory.

VI. SUMMARY

It has been shown that any of the methods described above give results which, though only approximate from a scientific standpoint, are satisfactorily accurate for practical purposes. The volatilization of the thinner, in some cases turpentine and in others mineral spirits, from drying films of freshly prepared varnishes was practically complete in two hours at room temperature (30 to 35° C).

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